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ASYMMETRIC BENT-CORE LIQUID CRYSTALS BASED ON 1,3-BIS-(4`-HYDROXYPHENYLAZO)BENZENE CENTRAL CORE

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ABSTRACT. The paper presents the synthesis and liquid-crystalline properties of some new asymmetric *bent-core* compounds based on a 1,3-bis-(4`-hydroxyphenylazo)benzene central core. The first class of asymmetric derivates were obtained by esterification of some hockey-stick derivates with 4-methoxybenzoic acid and the second one by estherification with 3-bromo-4-methoxybenzoic acid, in the presence of 4-dimethylaminopyridine (**DMAP**) and N,N'-d**icyclohexyl-carbodiimide (DCC). The** liquid crystalline properties were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The first class evidenced enantiotropic liquid crystalline properties, while the second one presented monotropic liquid crystalline behavior.

Keywords: *liquid crystals, asymmetric bent-core compounds*

INTRODUCTION

Liquid crystals (LCs) have been intensively investigated for about half a century and numerous important applications have been developed for them in modern technologies. For example, LC display panels and LC-based organic light emitters are widely used in the information display industry. Being a new member in the LC family, banana-shaped LCs have attracted intense attention because of their electro-optically switchable ferro- and antiferroelectricity although the individual molecules are achiral [1–5]. The relationship between the molecular structures and their mesomorphic properties is one of the most intensively studied topic for banana-shaped LCs. To study the influence of structural variations on mesomorphic properties and transition temperatures, different parts of the banana-shaped molecules have been varied and more than 1000 banana-shaped mesogens have been synthesized in the last years [6–10]. Since then, hundreds of *bent-core* compounds were synthesized and

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the structures of the banana phases were characterized with numerous analyzing techniques. A brief review of the literature reveals that most of the synthesized banana shaped LCs contain five benzene rings in their bent cores and the remaining banana-shaped LCs are composed of either four, six or seven benzene rings in their bent cores [11].

This paper presents the synthesis, structural characterization and mesomorphic behavior of two new asymmetric classes of bent core type compounds, which have as central core 1,3-bis-(4`-hydroxyphenylazo)benzene. The new compounds consist of six aromatic rings, connected *via* azo groups and esteric units of identical orientation. The asymmetry of molecules is caused by uneven distribution of the aromatic rings. For one series of the *bent-core* compounds one terminal aromatic ring presents a bromine atom as lateral substituent. The longer arm of the asymmetric compounds is ended with an alkoxy tail while the shorter arm ends with a methoxy group. Nine of the reported compounds present liquid crystalline properties under polarized optical microscopy (POM) and DSC investigation.

RESULTS AND DISCUSSION

Scheme 1 presents the total synthesis of the new asymmetric *bent-core* liquid crystals **4a-e** and **5a-e**. The first part of the synthesis depicts the synthesis of the phenolic intermediates **3a-e** which were obtained in our group for a previous work.

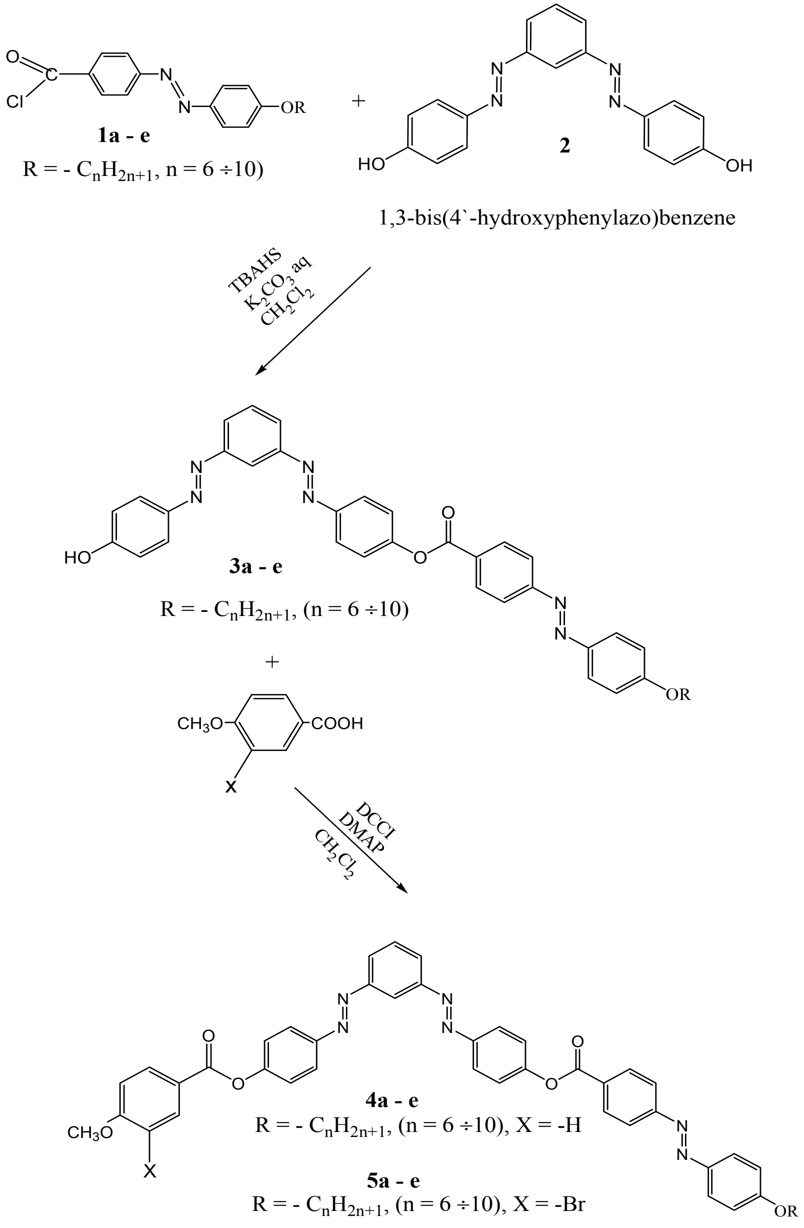
The central core, 1,3-bis-(4`-hydroxyphenylazo)benzene (**2**) was synthesized using diazotization and coupling reactions [12]. The azo aromatic acid chlorides (**1a-e**) were obtained by reacting the 4-(4-alkoxyphenylazo)-benzoic acids [15] with thionyl chloride [13].

The hockey-stick like compounds **3a-e** were obtained by reacting the 4-(4-alkoxyphenylazo)-benzoyl chlorides **1a-e** with 1,3-bis-(4`-hydroxyphenylazo) benzene (**2**) in a two-phase system dichloromethane / aqueous potassium carbonate and in the presence of tetrabutylammonium hydrogensulfate as phase transfer catalyst, at room temperature [14].

Finally, the esterification of **3a-e** compounds with 4-methoxybenzoic acid or 3-bromo-4-methoxybenzoic acid in the presence of DCC and DMAP, in anhydrous methylene chloride afforded the final *bent-core* compounds **4a-e** (in 35–73% yields) and, respectively, **5a-e** (in 37–60% yields).

Liquid-crystalline properties

Investigation by POM and DSC techniques of the mesomorphic properties of the asymmetric derivatives **4a-e** evidenced enantiotropic liquid-crystalline properties while for **5a-d** compounds the behavior was of monotropic type (compound **5e** did not present liquid crystalline properties). For the *bent-core* compounds **5a-d** the mesomorphic behavior is quite different, due to the presence of the bromo substituent on the aromatic ring. Thus, the stability of mesophases for compounds **4a-e** on cooling is superior if compared with compounds **5a-e**, which exhibited only monotropic mesophases. The types of mesophases were assigned by visual comparison with known phase standards. According to the literature data, the first series of banana-shaped compounds showed a B_6 mesophase [16].



Scheme 1

Table 1 presents the ranges of the stability of mesophases corresponding to compounds **4a-e** and **5a-e**.

Table 1. Range of mesophases for the asymmetric compounds **4a–e** / **5a-e**

Compounds		Range of mesophases (^{0}C)	
		On heating	On cooling
4a /5a	n=6	156-183^{0}C / -	169-105^{0}C / 166-151^{0}C
4b /5b	n=7	146-205^{0}C / -	200-132^{0}C / 179-156^{0}C
4c /5c	n=8	159-181^{0}C / -	177-112^{0}C / 166-152^{0}C
4d /5d	n=9	133-159^{0}C / -	138-67^{0}C / 159-150^{0}C
4e /5e	n=10	128-142^{0}C / -	137-122^{0}C / -

The results highlight the range of mesophase that is wider on cooling. The presence of the 4-methoxybenzoic acid as terminal unit have a positive influence, causing the increasing of the mesophase range (on heating from 14-59^{0}C and on cooling from 15-64^{0}C for compounds **4a-e**), but the introduction of a bromine atom as lateral substituent on the aromatic ring as in **5a-d** compounds cause the decreasing of mesophase stability between 9-23^{0}C, on cooling.

Both **4a-e** and **5a-e** derivatives showed a very good thermal stability, evidenced by thermal analysis studies, the T_{onset} values being situated with around 100^{0}C higher than the isotropisation temperatures. Generally, the thermal degradation of the asymmetric *bent-core* compounds of **4** and **5** type takes place in two stages, with the exception of **4a** or **5a** and **4d** compounds when the degradations occurs in one and three stages, respectively.

Tables 2 and 3 give the temperatures of the phase transitions determined by using differential scanning calorimetry and/or POM.

Table 2. Transition temperatures (°C) and transition enthalpies (ΔH / Jg^{-1}) for the bent-core compounds **4a-e**

Compounds		T / °C (ΔH / Jg^{-1})							T_{onset} (^{o}C)
		Heating (^{o}C)			Cooling (^{o}C)				
		K_1 / K_2	K_2/LC	LC / I	I /LC	LC/LC	LC/ K_2	K_2 / K_1	
4a	n=6	113 [0.70]	156 [-23.68]	183 [-0.36]	169 [1.83]	-	105 [23.97]	-	330
4b	n=7	125 [-15.92]	146 [-24.81]	205 [-2.41]	200 [6.22]	-	132 [31.85]	-	345
4c	n=8	131 [4.10]	158 [-31.82]	181 [-3.50]	177 [1.77]	-	112 [23.63]	-	341
4d	n=9	133*	-	159*	138*	124*	67*	48*	202
4e	n=10	-	128 [-13.92]	142 [-0.32]	137 [1.51]	-	122 [-1.76]	117 [3.99]	325

On the heating cycle, three endothermic peaks are present. The first one, at 125°C, is determined by the phenomenon of polymorphism and describes a crystalline-crystalline transition. The B_6 mesophase starts at 146°C, which is accompanied by a relatively large thermal effect (-24.81 J/g), and ends with the peak at 205°C. At this point the isotropisation occurred, and the peak is accompanied by a small thermal effect. On the cooling cycle it can be observed the presence of two exothermic peaks. One at 200^{0}C, caused by the isotropic-liquid crystalline transition, and the prominent peak at 132^{0}C which corresponds to the liquid crystal-crystalline transition.

The presence of bromine atom in the structure of **5a-e** compounds does not favorable influence the liquid crystalline behavior. Compounds **5a-e** evidenced only a monotropic behavior, with narrow intervals of stabilities of the mesophases (Table 1).

Table 3. Transition temperatures (°C) and transition enthalpies (ΔH / Jg^{-1}) for the bent-core compounds **5a-e**

Compounds		T / °C (ΔH / Jg^{-1})						T_{onset} (°C)
		Heating (^{o}C)		Cooling (^{o}C)				
		K_1/K_2	K_2/I	I /LC	LC/ K_3	K_3 / K_2	K_2 / K_1	
5a	n=6	-	175 [-33.45]	166 [0.38]	151 [3.59]	147 [4.63]	-	333
5b	n=7	133 [-8.52]	172*	179 [1.60]	156 [5.75]	119 [6.68]	80 [2.09]	304
5c	n=8	-	176*	166*	152*	-	-	337
5d	n=9	158 [-25.91]	166 [-0.29]	159 [0.47]	150 [-26.07]	65 [0.34]	-	337
5e	n=10	-	168*	-	-	154 [28.45]	121 [0.41]	336

Abbreviations: K – crystalline; LC – liquid crystal; I – isotropic; T_{onset} – the initial temperature of thermal degradation; * Data obtained from POM investigations

Figure 1 presents, as an example, the DSC curves of compound **4b**.

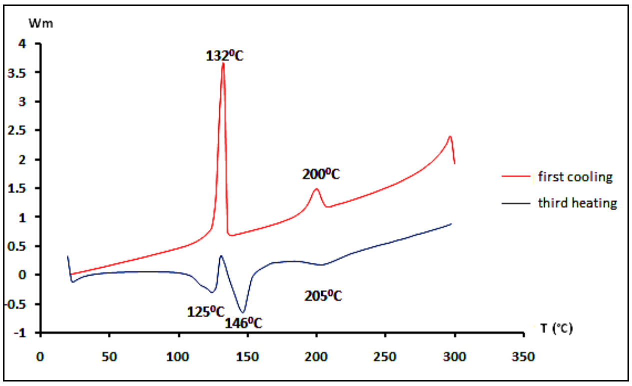


Figure 1. The DSC curves of compound **4b**

As an example, according to POM data, the mesophase for compound **5c** begins, on cooling, at 166°C and ends at 152°C when the crystallization occurred.

Figure 2 presents the textures observed by polarized optical microscopy upon heating and cooling cycles for compound **4b**.

Figure 3 depicts, as an example, the DSC curves of compound **5c** and Figure 4 presents the textures observed by polarized optical microscopy upon cooling for compounds **5a** and **5c**.


(a) (b) (c)

Figure 2. Thermal optical micrographs of the texture displayed by compound 4b: (a) 171^{0}C, first cooling; (b) 167^{0}C, second cooling; (d) 196^{0}C, third heating.

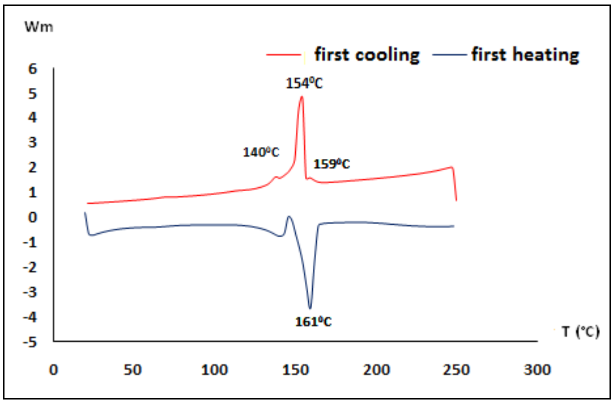


Figure 3. The DSC curves of compound **5c**


(a) (b)

Figure 4. Thermal optical micrographs of the textures displayed by compounds **5a** and **5c** on first cooling: a) **5a**, 157^{0}C and b) **5c**, 157^{0}C.

CONCLUSIONS

Two new series of *bent-core* liquid crystals based on a 1,3-disubstituted core have been synthesized and their mesomorphic properties have been investigated. ^{1}H-NMR and ^{13}C-NMR were used for structural characterization while the liquid crystalline behavior was confirmed by differential scanning calorimetry and optical polarizing microscopy. The liquid crystalline behavior was of enantiotropic or monotropic type, depending on the structure of the asymmetric compounds. The assigned mesophases were of smectic type. The obtained compounds showed a very good thermal stability in the mesophase domain.

EXPERIMENTAL SECTION

MATERIALS

Analytical reagents and solvents were provided either by Aldrich (Germany), or by Merck (Germany), and were used without further purification. Silica gel 60 (Merck) was used for column chromatography (CC). Thin-layer chromatography (TLC) was performed on silica gel plates (Merck, silica gel F_{254}). 4-((3-((4-Hydroxyphenyl)azo)phenyl)azo)phenyl 4-((4-alkyloxyphenyl) azo) benzoates were synthesized in our laboratory for a previous work [12-15].

INSTRUMENTATION

Confirmation of the structures of the intermediates and final products was obtained by ^{1}H-NMR and ^{13}C-NMR, using a Bruker Avance DRX 400 MHz spectrometer (Rheinstein, Germany) with tetramethylsilane as internal standard. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard.

Transition temperatures were determined using a Linkam heating stage and Linksys 32 temperature control unit (Surrey, BC, Canada) in conjunction with a Axioscop 40 Zeiss polarizing optical microscope (Jena, Germany) and Qimaging/Retiga-1000R camera for image capture (Surrey, BC, Canada), the transitions being confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10^{0}C/min under nitrogen atmosphere, with sample measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

All thermal analyses were performed on a Mettler-Toledo TGA SDTA851^e derivatograph in an N_2 atmosphere, with a flow rate of 20mL/min and a heating rate of 10^{0}C/min from 25^{0}C to 900^{0}C. In order to obtain comparable data, constant operational parameters were kept for all samples.

SYNTHESIS

General method for the synthesis of the asymmetric bent-core liquid crystals 4a-e

A mixture of 1 equiv. of asymmetric compounds **(3a-e)**, 1.1 equiv. of 4-methoxybenzoic acid, and 1.5 equiv. of DMAP, dissolved in dry CH_2Cl_2, was stirred for a few minutes and then 1.8 equiv. of DCC dissolved in dry dichloromethane was added dropwise. The reaction mixture was stirred for 72 h at room temperature and then the precipitated N,N`-dicyclohexylurea (DCCU) was filtered off. The solvent was evaporated in vacuum and the solid was chromatographed on silicagel using a 20/1 mixture of dichloromethane/ ethyl acetate as eluent.

4-((3-((4-(4-((4-hexyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 4-methoxybenzoate (4a): Quantities: compound **(3a)** (0.190 g; 0.30 mmol), 4-methoxybenzoic acid (0.05 g; 0.33 mmol), DCC (0.112g; 0.54 mmol), DMAP (0.055 g; 0.45 mmol), 100 ml dry dichloromethane. Orange product, η = 47.82 % (0.110 g), liquid crystal: 113^0C (K/K), 156^0C (K/CL), 183^0C (CL/I), 169^0C (I/CL), 105^0C (CL/K) .^{1}H-RMN δ_H ppm ($CDCl_3$): 8.45 (m, 1H, Ar), 8.35 (d, 2H, Ar, J=8.33 Hz), 8.18 (d, 2H, Ar, J=8.55 Hz), 8.05 (m, 6H, Ar), 7.96 (m, 4H, Ar), 7.65 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.55 Hz), 7.40 (d, 2H, Ar, J=8.55 Hz), 7.00 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2), 3.89 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.49 (cv, 2H, -CH_2), 1.34 (m, 4H, -CH_2), 0.92 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.53, 164.38, 164.11, 162.55, 155.96, 153.45, 153.37, 153.35, 153.22, 150.27, 150.10, 146.88, 132.41, 131.30, 130.09, 129.68, 125.43, 125.39, 125.35, 124.39, 124.33, 122.60, 122.53, 122.44, 121.54, 116.52, 114.86, 113.95 (2* >C=O esteric + 26C, aromatic); 68.61 (-O-CH_2), 55.55 (OCH_3), 31.59, 29.21, 25.72, 22.59, 13.97 (5C, aliphatic).

4-((3-((4-(4-((4-heptyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 4-methoxybenzoate (4b): Quantities: compound **(3b)** (0.200 g; 0.31 mmol), 4-methoxybenzoic acid (0.052 g; 0.34 mmol), DCC (0.116g; 0.56 mmol), DMAP (0.057 g; 0.46 mmol), 100 ml dry dichloromethane. Orange product, η = 41.49 % (0,100 g), liquid crystal: 125^0C (K/K), 146^0C (K/CL), 205^0C (CL/I), 200^0C (I/CL), 132^0C (CL/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.45 (m, 1H, Ar), 8.34 (d, 2H, Ar, J=8.55 Hz), 8.17 (d, 2H, Ar, J=8.55 Hz), 8.06 (m, 6H, Ar), 7.96 (m, 4H, Ar), 7.66 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.77 Hz), 7.40 (d, 2H, Ar, J=8.77 Hz), 7.00 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2), 3.89 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.34 (m, 6H, -CH_2), 0.91 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.52, 164.37, 164.20, 162.63, 156.09, 153.57, 153.51, 153.48, 153.34, 150.38, 150.22, 147.04, 132.43, 131.30, 130.21, 130.07, 129.67, 125.36, 125.22, 124.40, 124.33, 122.63, 122.51, 122.44, 121.70, 116.66, 114.95, 114.02 (2* >C=O esteric + 26C, aromatic); 68.57 (-O-CH_2), 55.55 (OCH_3), 31.79, 29.23, 29.05, 26.01, 22.61, 14.04 (6C, aliphatic).

4-((3-((4-(4-((4-octyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 4-methoxybenzoate (4c): Quantities: compound **(3c)** (0.160 g; 0.24 mmol), 4-methoxybenzoic acid (0.04 g; 0.26 mmol), DCC (0.09g; 0.44 mmol), DMAP (0.044 g; 0.36 mmol), 100 ml dry dichloromethane. Orange product, η = 72.91 % (0.140 g), liquid crystal: 131^{0}C (K/K), 158^{0}C (K/CL), 181^{0}C (CL/I), 177^{0}C (I/CL), 112^{0}C (CL/K).^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.18 (d, 2H, Ar, J=8.77 Hz), 8.07 (m, 6H, Ar), 7.97 (m, 4H, Ar), 7.67 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.77 Hz), 7.40 (d, 2H, Ar, J=8.76 Hz), 7.01 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2), 3.90 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.30 (m, 10H, -CH_2), 0.90 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.53, 164.38, 164.10, 162.55, 155.95, 153.45, 153.36, 153.34, 153.22, 150.25, 150.10, 146.88, 132.41, 131.30, 130.08, 129.68, 125.43, 129.39, 125.35, 124.38, 124.33, 122.60, 122.53, 122.44, 121.52, 116.52, 114.85, 113.95 (2* >C=O esteric + 26C, aromatic), 68.48 (-O-CH_2-), 55.54 (OCH_3), 31.81, 29.35, 29.23, 29.17, 26.01, 22.66, 14.10 (7C, aliphatic).

4-((3-((4-(4-((4-nonyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 4-methoxybenzoate (4d): Quantities: compound **(3d)** (0.200 g; 0.30 mmol), 4-methoxybenzoic acid (0.05 g; 0.33 mmol), DCC (0.111g; 0.54 mmol), DMAP (0.054 g; 0.45 mmol), 100 ml dry dichloromethane. Orange product, η = 35.41 % (0.085 g), liquid crystal: 133^{0}C (K/K), 159^{0}C (CL/I), 138^{0}C (I/CL), 124^{0}C (CL/CL), 67^{0}C (CL/K), 48^{0}C (K/K) .^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.17 (d, 2H, Ar, J=8.77 Hz), 8.07 (m, 6H, Ar), 7.97 (m, 4H, Ar), 7.67 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.55 Hz), 7.40 (d, 2H, Ar, J=8.55 Hz), 7.01 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2), 3.90 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.28 (m, 10H, -CH_2), 0.89 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.54, 164.39, 164.11, 162.54, 155.95, 153.44, 153.34, 153.22, 150.25, 150.10, 146.86, 132.41, 131.30, 130.53, 130.07, 129.68, 125.35, 125.19, 124.38, 124.33, 122.60, 122.53, 122.44, 122.30, 121.52, 116.52, 114.85, 113.95 (2 * >C=O esteric + 26C, aromatic); 68.48 (-O-CH_2), 55.54 (OCH_3), 31.88, 29.52, 29.39, 29.26, 29.18, 26.01, 22.67, 14.12 (8C, aliphatic).

4-((3-((4-(4-((4-decyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 4-methoxybenzoate (4e): Quantities: compound **(3e)** (0.200 g; 0.29 mmol), 4-methoxybenzoic acid (0.049 g; 0.32 mmol), DCC (0.109 g; 0.53 mmol), DMAP (0.051 g; 0.42 mmol), 100 ml dry dichloromethane. Orange product, η = 37.65 % (0,09 g), liquid crystal: 128^{0}C (K/CL), 142^{0}C (CL/I), 137^{0}C (I/CL), 122^{0}C (CL/K), 117^{0}C (K/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.36 (d, 2H, Ar, J=8.55 Hz), 8.18 (d, 2H, Ar, J=8.77 Hz), 8.07 (m, 6H, Ar), 7.98 (m, 4H, Ar), 7.68 (m, 1H, Ar), 7.445 (d, 2H, Ar, J=8.77 Hz), 7.40 (d, 2H, Ar, J=8.55 Hz), 7.02 (m, 4H, Ar), 4.06 (t, 2H, -O-CH_2), 3.91 (s, 3H, -OCH_3), 1.83 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.28 (m, 12H, -CH_2), 0.89 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.55, 164.39, 164.09, 162.54, 155,96, 153.44, 153.36, 153.34, 153,20, 150.26, 150.09, 146.88, 132.41, 131.30, 130.08, 129.68, 125.44, 125.41, 125.34, 124.59, 124.32, 122.59, 122.52, 122.45, 121.51, 116.49, 114.85, 113.95 (2 * >C=O esteric + 26C, aromatic); 68.48 (-O-CH_2), 55.54 (OCH_3), 31.89, 29.70, 29.56, 29.37, 29.31, 29.16, 26.00, 22.68, 14.11 (9C, aliphatic).

General method for the synthesis of the asymmetric bent-core liquid crystals 5a-e

A mixture of 1 equiv. compounds **(3a-e)**, 1.1 equiv. of 3-bromo-4-methoxybenzoic acid, and 1.5 equiv. of DMAP, dissolved in dry CH_2Cl_2, was stirred for a few minutes and then 1.8 equiv. of DCC dissolved in dry dichloromethane was added dropwise. The reaction mixture was stirred for 48 h at room temperature and then the precipitated N,N`- dicyclohexylurea (DCCU) was filtered off. The solvent was evaporated in vacuum and the solid chromatographed on silicagel using a 20/1 mixture of dichloromethane/ethyl acetate as eluent.

4-((3-((4-(4-((4-hexyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 3-bromo-4-methoxybenzoate (5a): Quantities: compound **(3a)** (0.175 g, 0.28 mmoli), 3-bromo-4-methoxybenzoic acid (0.071 g, 0.30 mmoli), DCC (0.103 g, 0.5 mmoli), DMAP (0.051g, 0.42 mmoli), 100 ml dry dichloromethane. Orange product, η = 42.73 % (0.100 g), liquid crystal: 175^0C (K/I), 166^0C (I/CL), 151^0C (CL/K), 147^0C (K/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.45 (m, 1H, Ar), 8.40 (d, 1H, Ar, J=1.97 Hz), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.16 (dd, 1H, Ar, J_1=8.55 Hz, J_2=1.97 Hz), 8.06 (m, 6H, Ar), 7.97 (m, 4H, Ar), 7.68 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.77 Hz), 7.39 (d, 2H, Ar, J=8.77 Hz), 7.02 (d, 2H, Ar, J=8.99 Hz), 6.985 (d, 1H, Ar, J=8.99 Hz), 4.05 (t, 2H, $-O-CH_2$), 3.99 (s, 3H, $-OCH_3$), 1.82 (cv, 2H, $-CH_2$), 1.49 (cv, 2H, $-CH_2$), 1.35 (m, 4H, $-CH_2$), 0.92 (t, 3H, $-CH_3$). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.36, 163.41, 162.51, 160.20, 155.92, 153.36, 153.30, 153.19, 153.10, 150.21, 150.18, 146.84, 135.39, 131.42, 131.27, 130.04, 129.67, 125.44, 125.32, 124.36, 124.32, 122.69, 122.58, 122.42, 122.39, 116.48, 114.82, 111.22 (2*>C=O esteric + 26C, aromatic); 68.48 ($-O-CH_2$), 56.56 (OCH_3), 31.57, 29.13, 25.69, 22.59, 14.04 (5C, aliphatic).

4-((3-((4-(4-((4-heptyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 3-bromo-4-methoxybenzoate (5b): Quantities: compound **(3b)** (0.170 g, 0.27 mmoli), 3-bromo-4-methoxybenzoic acid (0.067 g, 0.29 mmoli), DCC (0.098 g, 0.47 mmoli), DMAP (0.048 g, 0.39 mmoli), 100 ml dry dichloromethane. Orange product, η = 59.73 % (0.135 g), liquid crystal: 133^0C (K/K), 172^0C (K/I), 179^0C (I/CL), 156^0C (CL/K), 119^0C (K/K), 80^0C (K/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.40 (d, 1H, Ar, J=8.55 Hz), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.17 (dd, 1H, Ar, J_1=8.55 Hz, J_2=1.97 Hz), 8.12 (m, 6H, Ar), 8.00 (m, 4H, Ar), 7.70 (m, 1H, Ar), 7.49 (d, 2H, Ar, J=8.77 Hz), 7.43 (d, 2H, Ar, J=8.77 Hz), 7.02 (d, 2H, Ar, J=8.99 Hz), 6.98 (d, 1H, Ar, J=8.99 Hz), 4.06 (t, 2H, $-O-CH_2$), 3.95 (s, 3H, $-OCH_3$), 1.83 (cv, 2H, $-CH_2$), 1.53 (cv, 2H, $-CH_2$), 1.38 (m, 6H, $-CH_2$), 0.95 (t, 3H, $-CH_3$). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.39, 163.44, 162.53, 160.23, 155.94, 153.43, 153.32, 153.20, 153.12, 150.24, 150.20, 150.09, 146.86, 135.40, 131.43, 131.29, 130.05, 129.68, 125.45, 125.34, 124.37, 124.31, 122.58, 122.52, 122.44, 116.47, 114.84, 113.93 (2 * >C=O esteric + 26C, aromatic); 68.47 ($-O-CH_2$), 56.56 (OCH_3), 31.75, 29.15, 29.04, 25.95, 22.59, 14.07 (6C, aliphatic).

4-((3-((4-(4-((4-octyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 3-bromo-4-methoxybenzoate (5c): Quantities: compound **(3c)** (0.200 g, 0.30 mmoli), 3-bromo-4-methoxybenzoic acid (0.077 g, 0.33 mmoli), DCC

(0.113 g, 0.55 mmoli), DMAP (0.056 g, 0.46 mmoli), 100 ml dry dichloromethane. Orange product, η = 45.45 % (0.120 g), liquid crystal: 176^0C (CL/I), 166^0C (I/CL), 152^0C (CL/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.42 (d, 1H, Ar, J=1.97 Hz), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.16 (dd, 1H, Ar, J_1=8.55, J_2=1.97), 8.07 (m, 6H, Ar), 7.98 (m, 4H, Ar), 7.68 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.77 Hz), 7.39 (d, 2H, Ar, J=8.77 Hz), 7.02 (d, 2H, Ar, J=8.55 Hz), 6.99 (d, 1H, Ar, J=8.55 Hz), 4.05 (t, 2H, -O-CH_2), 3.99 (s, 3H, -OCH_3), 1.83 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.34 (m, 8H, -CH_2), 0.90 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.37, 163.42, 162.53, 160.23, 155.95, 153.43, 153.32, 153.21, 153.13, 150.24, 150.20, 150.09, 146.87, 135.40, 132.40, 131.42, 131.29, 130.06, 129.68, 125.43, 125.34, 124.37, 122.58, 122.52, 122.43, 116.50, 114.84, 113.94 (2 * >C=O esteric + 26C, aromatic); 68.47 (-O-CH_2), 55.53 (OCH_3), 31.80, 29.34, 29.22, 29.15, 26.00, 22.64, 14.09 (7C, aliphatic).

4-((3-((4-(4-((4-nonyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo)phenyl 3-bromo-4-methoxybenzoate (5d): Quantities: compound **(3d)** (0.240 g, 0.36 mmoli), 3-bromo-4-methoxybenzoic acid (0.091 g, 0.39 mmoli), DCC (0.133 g, 0.64 mmoli), DMAP (0.058 g, 0.47 mmoli), 100 ml dry dichloromethane. Orange product, η = 41.13 % (0.130 g), liquid crystal: 158^0C (K/K), 166^0C (K/I), 159^0C (I/CL), 150^0C (CL/K), 65^0C (K/K). ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.42 (d, 1H, Ar, J=1.97 Hz), 8.355 (d, 2H, Ar, J=8.34 Hz), 8.16 (dd, 1H, Ar, J_1=8.55 Hz, J_2=1.97 Hz), 8.07 (m, 6H, Ar), 7.98 (m, 4H, Ar), 7.68 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8.56 Hz), 7.40 (d, 2H, Ar, J=8.56 Hz), 7.02 (d, 2H, Ar, J=8.55 Hz), 6.99 (d, 1H, Ar, J=8.55 Hz), 4.05 (t, 2H, -O-CH_2), 4.00 (s, 3H, -OCH_3), 1.83 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.28 (m, 10H, -CH_2), 0.89 (t, 3H, -CH_3). ^{13}C-RMN δ_C ppm ($CDCl_3$): 164.38, 163.43, 162.53, 160.23, 155.94, 153.43, 153.32, 153.21, 153.13, 150.20, 150.09, 146.87, 135.40, 132.40, 131.42, 131.29, 130.06, 129.68, 125.49, 125.34, 124.37, 124.31, 122.58, 122.52, 122.43, 116.50, 114.84, 113.94 (2 * >C=O esteric + 26C, aromatic); 68.47 (-O-CH_2), 55.53 (OCH_3), 31.87, 29.52, 29.37, 29.25, 29.15, 25.99, 22.66, 14.10 (8C, aliphatic).

4-((3-((4-(4-((4-decyloxyphenyl)azo)benzoyloxy)phenyl)azo)phenyl)-azo) phenyl 3-bromo-4-methoxybenzoate (5e): Quantities: compound **(3e)** (0.33 g, 0.48 mmoli), 3-bromo-4-methoxybenzoic acid (0.122 g, 0.53 mmoli), DCC (0.179 g, 0.87 mmoli), DMAP (0.088 g, 0.72 mmoli), 100 ml dry dichloromethane. Orange product, η = 37.03 % (0.160 g), m.p=168^0C. ^{1}H-RMN δ_H ppm ($CDCl_3$): 8.46 (m, 1H, Ar), 8.40 (m, 1H, Ar, J=1.97 Hz), 8.35 (d, 2H, Ar, J=8.55 Hz), 8.17 (dd, 1H, Ar, J_1=8.77 Hz, J_2=1.97 Hz), 8.07 (m, 6H, Ar), 7.97 (m, 4H, Ar), 7.68 (m, 1H, Ar), 7.44 (d, 2H, Ar, J=8,77 Hz), 7.395 (d, 2H, Ar, J=8.77 Hz), 7.02 (m, 2H, Ar, J=8.77 Hz), 6.98 (d, 1H, Ar, J=8.55 Hz), 4.05 (t, 2H, -O-CH_2), 3.99 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.48 (cv, 2H, -CH_2), 1.28 (m, 12H, -CH_2), 0.89 (t, 3H, -CH_3).^{13}C-RMN δ_C ppm ($CDCl_3$): 164.38, 163.43, 162.53, 160.23, 155.94, 153.42, 153.33, 153.30, 153.21, 153.12, 150.20, 150.07, 146.86, 135.41, 132.40, 131.41, 131.29, 130,06, 129.68, 125.49, 125.34, 124.37, 122.58, 122.52, 122.44, 116.49, 114.84, 113.93 (2 * >C=O esteric + 26C, aromatic); 68.46 (-O-CH_2), 55.52 (OCH_3), 31.88, 29.67, 29.54, 29,36, 29.31, 29.15, 25.99, 22.66, 14.10 (9C, aliphatic).

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